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(54) **Heat insulation panels manufactured from modified polyisocyanurate foams**

(57) Heat insulation panels made from plates and the modified polyisocyanurate foams provided by a reaction of a polyisocyanate with a polyol composition mixture comprising a polyol, water, a trimerization catalyst, a carbodiimide catalyst, and an aromatic compound used as a chain extender. An amount of the aromatic compound used in the preparation is 0.5 to 10.0 % by weight with respect to a total weight of the polyisocyanate and the polyol mixture.

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Description

TECHNICAL FIELD

5 The present invention pertains to the manufacture of heat insulation (hereinafter insulation) panels comprising plates and modified polyisocyanurate foams, as insulation materials, provided by reacting a polyisocyanate, a polyol, an aromatic compound, and water in the presence of a carbodiimide catalyst and a trimerization catalyst.

BACKGROUND ART

10 The preparation of modified polyisocyanurate foams containing isocyanurate (a trimer of isocyanate) and carbodiimide linkages is well known in the art as disclosed by U.S. Pat. No. 3,657,161. Further arts such as U.S. Pat. Nos. 3,894,972; 3,928,256; 3,981,829; 3,998,766; and 4,166,164 disclose other well known catalysts: (i) furfuryl alcohols and a tertiary amine trimerization catalyst, (ii) a co-catalyst system of tertiary aminoalcohols and a tertiary amine trimerization catalyst, (iii) a catalyst system comprising alkanol amino triazine, hexahydrotriazine, and phenol or substituted phenol, (iv) oxyalkylated Mannich polyols, and (v) C₁-C₈ alkali metal carboxylates as trimerization catalysts.

15 In general, the modified polyisocyanurate foams produced in these preparations have high friability and poor flame-retardancy for insulation materials. Thus phosphorous compounds containing active hydrogen have been employed to improve the flame-retardancy of the foams, as disclosed in U.S. Pat. No. 3,994,893. The use of toluene diisocyanate has been employed in order to improve the friability and flame-retardancy of the foams and is described in U.S. Pat. No. 3,994,837.

20 In the foregoing preparations, chlorofluorocarbons were used as blowing agents. However, due to the prohibited use of chlorofluorocarbons in near future, processes of the preparation of the foams without the use of chlorofluorocarbons have been proposed in the arts disclosed by European Patent Publication EP 0381 324 A1 and U.S. Pat. No. 5,126,305. These arts describe the use of phospholene oxides as carbodiimide catalysts and water so as to form carbon dioxide as a blowing agent. Unfortunately, the employment of water brings urea linkages which are spread unevenly and cause coagulation or domain in the foams. Thus the foams provided by these processes were friable and possessed insufficient adhesion strength for insulation materials.

DISCLOSURE OF THE INVENTION

25 The present invention relates to the manufacture of insulation panels using the modified polyisocyanurate foams as insulation materials. Insulation panels made from the foams are often used as construction materials such as building walls and roofs of warehouses and factories. Thus the panels are required to have low friability, high compression strength, excellent flame-retardancy, and, particularly, high adhesion to plates of the insulation panels.

The present invention involves the use of aromatic compounds in addition to the prior art process. The aromatic compounds are used as chain extenders to form hard segments which are scattered at molecular level as firm branches in polymer chains of the foams. Therefore, the use of the aromatic compounds enables to improve not only adhesion strength but also compression strength and friability of the foams.

30 A foam reaction system contains a polyisocyanate and a polyol composition mixture comprising a polyol, an aromatic compound, water, a trimerization catalyst, and a carbodiimide catalyst. A suitable amount of the aromatic compound is 0.5 to 10.0 wt %, which is calculated based upon a total amount of the polyol mixture and the isocyanate. An amount of water in the present invention is typically 0.5 to 1.5 wt % based on the total weight of the reaction system. A foam reaction is obtained simply by adding the polyisocyanate to the polyol mixture. This admixture is injected between metal plates separated with space and allowed for foaming, in resulting that the foamed admixture adheres to the plates.

35 Moreover, the insulation panels are manufactured by using carbon dioxide as a blowing agent, allowing no use of chlorofluorocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

40 FIG. 1 is a cross sectional view of a mechanical system of manufacturing insulation panels from modified polyisocyanurate foams prepared in the present invention;

FIG. 2 is a perspective view of a coating gantry injecting a mixture of starting materials space between plates and double conveyers adjusting the space; and

45 FIG. 3, composed of FIG. 3 (a) and FIG. 3 (b), illustrates a cross sectional view of an insulation panel comprising a male end, a female end, and a plastic foam sealant in FIG. 3 (a); and a cross sectional view of the insulation panel connected in series with other insulation panels in FIG. 3 (b).

DESCRIPTION OF THE INVENTION

In accordance with the present invention, modified polyisocyanurate foams are provided by a reaction of a polyisocyanate in the presence of a polyol composition mixture comprising aromatic compounds, trimerization catalysts, carbodiimide catalysts, and water. The use of the aromatic compounds is the essence of the present invention, and the compounds are used as chain extenders to improve adhesion strength, compression strength, and friability of the foams. The trimerization catalyst promotes the formation of isocyanurate linkages whereas the carbodiimide catalyst promotes the formation of carbodiimide linkages, associating with evolution of carbon dioxide. Also, another carbon dioxide is formed in a reaction of the polyisocyanate with water. As mentioned previously, these carbon dioxides are used as a blowing agent in the preparation, thus without using environmentally unsafe chlorofluorocarbons.

Details of the starting materials listed above are described in the following.

Suitable polyisocyanates used in the present invention are aliphatic, alicyclic, and aromatic polyisocyanates. It may be possible to use polyisocyanates having a combination of these groups. It is also plausible to employ polyisocyanates used in the preparations of polyurethanes and polyisocyanurates.

It is preferred to use aromatic diisocyanates such as 2,4-toluene diisocyanate (2,4-TDI), 2,6-toluene diisocyanate (2,6-TDI), crude toluene diisocyanate (crude-TDI), 4,4'-diphenyl methane diisocyanate (pure-MDI), and polymethylene polyphenyl polyisocyanate (crude-MDI); aromatic triisocyanates such as 4,4',4''-triphenyl methane triisocyanate and 2,4,6-toluene triisocyanate; aromatic tetraisocyanates such as 4,4'-dimethyl diphenyl methane-2,2'-5,5'-tetraisocyanate; aliphatic isocyanates such as hexamethylene-1,6-diisocyanate; alicyclic isocyanates such as hydromethylene diphenyl-diisocyanate; and others such as m-phenylene diisocyanate, naphthalene-1,5-diisocyanate, 1-methoxyphenyl-2,4-diisocyanate, 4,4'-biphenyl diisocyanate, 3,3'-dimethoxyl-4,4'-biphenylene diisocyanate, and 3,3'-dimethyldiphenyl methane-4,4'-diisocyanate.

It is most preferred to use 2,4-TDI, 2,6-TDI, crude-TDI, pure-MDI, crude-MDI, hexamethylene-1,6-diisocyanate, and hydromethylene diphenyldiisocyanate.

Suitable polyols used in the present invention are selected from aliphatic, saccharide, and aromatic polyols; it is suitable to use polyols with a combination of these groups. Such polyols are polyether polyols, polyester polyols, ester oils, and the like. It is also suitable to use either high or low molecular polyols that are normally used for the preparation of polyurethanes.

The polyether polyols are prepared, for example, by the addition of alkylene oxide to active hydrogen containing compounds such as polyalcohols, polyphenols, amines, and polycarboxylic acids.

Suitable polyalcohols for the preparation of the polyether polyols are diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6 hexadiol, diethylene glycol, and n-pentylglycol; and triols such as glycerin, pentaerythritol, and sucrose.

Suitable polyphenols for the preparation of the polyether polyols are pyrogallol, hydroquinone, bisphenol A, and a condensation product of phenol and formaldehyde.

Suitable amines for the preparation of the polyether polyols are ammonia; alcohol amines such as monoethanol amine, diethanol amine, triethanol amine, isopropanol amine, and amino ethyl ethanol amine; alkyl amines containing an C₁-C₂₂ alkyl group; aromatic amines such as diamines containing an C₂-C₆ alkylene group, polyalkylene amines, aniline, phenylene diamine, diamino toluene, xylene diamine, methylene dianiline, and diphenylether diamine; alicyclic amines such as isophorone diamine cyclohexylene diamine, and heterocyclic amines.

Suitable carboxylic acids for the preparation of the polyether polyol are alicyclic polycarboxylic acids such as succinic, adipic, sebacic, maleic, and dimer acids; and aromatic polycarboxylic acids such as phthalic, terephthalic, trimellitic, and pyromellitic acids.

More than two kinds of these active hydrogen containing compounds are used in the preparation of polyether polyols.

The alkylene oxide added to the active hydrogen containing compounds may be any one of propylene oxide, ethylene oxide, butylene oxide, and tetrahydrofuran. If more than two kinds of these alkylene oxides are used, they may be either block or random-added to the active hydrogen containing compounds.

Any suitable polyester polyols are used as polyols in the present invention, but it is preferred to use condensed polyester polyols prepared from polyalcohols (such as the diols listed above, trimethylol propane, and glycerin) and polycarboxylic acids (the ones listed above); polyester polypolyols prepared from the ring-opening polymerization of lactones; polyester polyols prepared from the addition of ethylene oxide adducts of nonyl phenol to scrap polyesters.

Most preferred polyols are aromatic, aliphatic, aromatic or aliphatic amine, pentaerythritol, or saccharide polyether polyols; aromatic or aliphatic carboxylic acid polyester polyols; and lactic polyester polyols.

The suitable and preferred polyols have their hydroxyl value ranges: generally, from 20 to 600 mg KOH/g; preferably, from 25 to 500 mg KOH/g; and, most preferably, from 50 to 400 mg KOH/g.

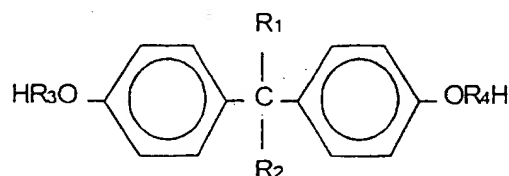
More than two kinds of these polyols may be used in the present invention.

Suitable aromatic compounds used in the present invention play an important role as chain extenders for the preparation of the modified polyisocyanurate foams. In the foam reaction, the aromatic compounds react with the polyisocyanate, resulting in the formation of hard segments in polymer chains of the foams. Cross linkers are often used to increase the cross linkage density of the foams, in resulting increases of compression strength and bending strength but an

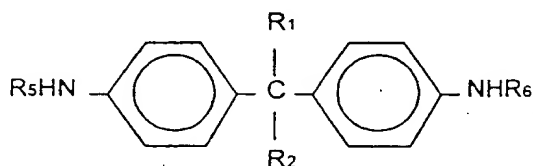
increase of flexibility and an a decrease of adhesion strength. On the other hand, the chain extenders improve not only the compression and bending strengths but also the friability and the adhesion strength.

The aromatic compounds are represented by the following formulae (I) and (II):

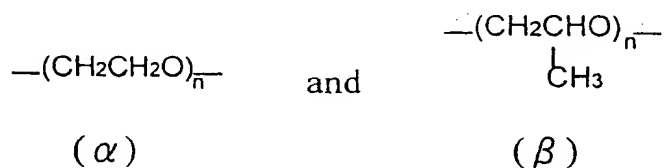
(I)



(II)



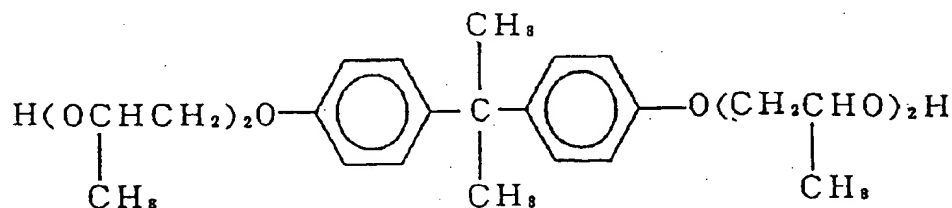
wherein R_1 and R_2 represent one of H and $-CH_3$, R_3 and R_4 represent one of the following (α) and (β):



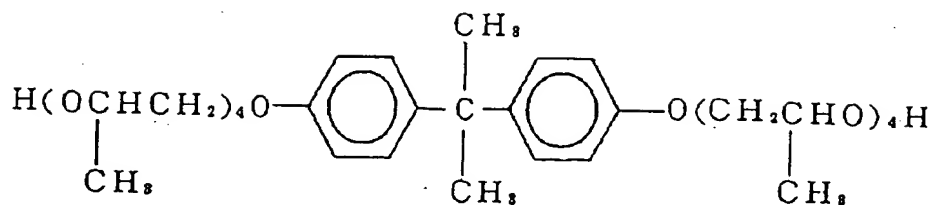
R_5 and R_6 represent C_1 - C_4 alkyl groups, and n represents an integer from 1 to 4.

In particular, it is most preferred to use the following aromatic compounds represented by (I-a), (I-b), (I-c), and (II-a):

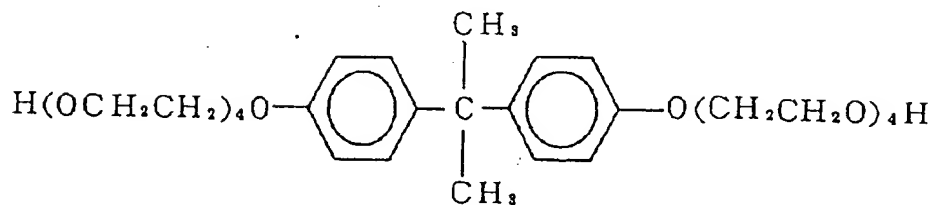
(I-a)



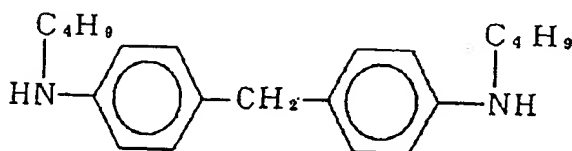
(I-b)



(I-c)

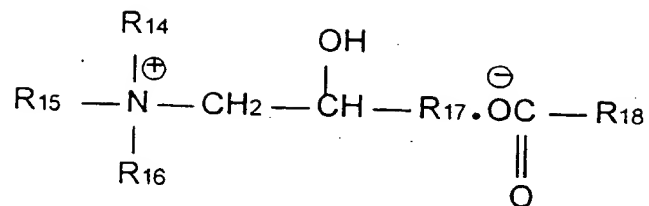


(II-a)



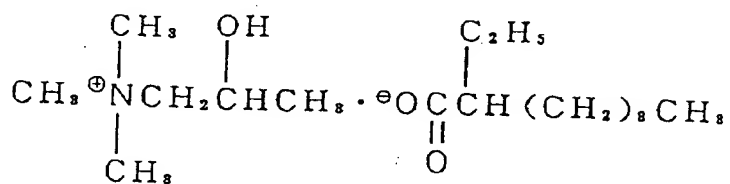
Suitable trimerization catalysts used are hydroxyl alkyl quaternary ammonium compounds which are normally used in the preparation of polyisocyanurate resins or polyurethane polyisocyanurate resins. These compounds are described in U.S. Pat No. 4,040,992.

The trimerization catalysts in this invention are the following quaternary ammonium salts represented by the formula (V):

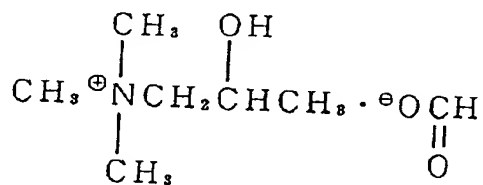


wherein R_{14} , R_{15} , and R_{16} represent alkyl groups, R_{17} and R_{18} represent one of hydrogen and alkyl groups.
It is preferred to use quaternary ammonium compounds from (V-a) to (v-l):

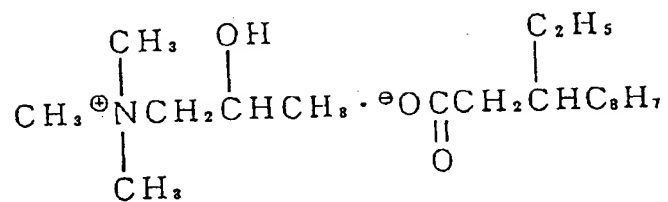
(V-a)



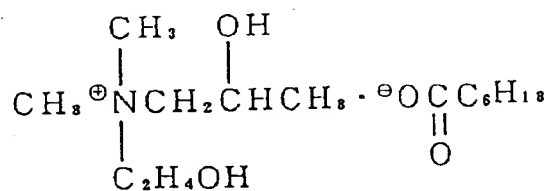
(V-b)



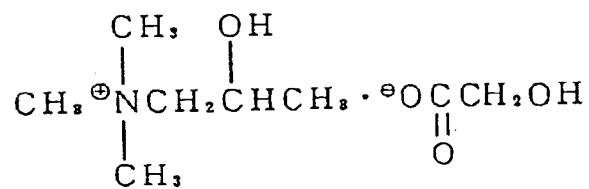
(V-c)



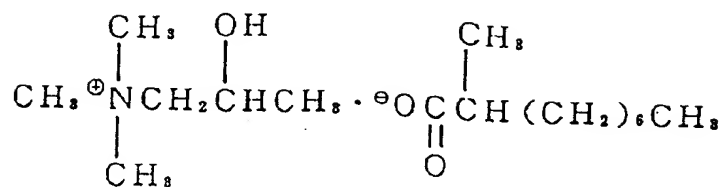
(V-d)



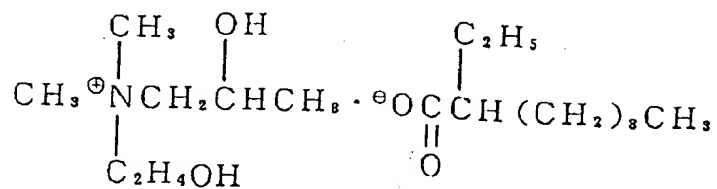
(V-e)



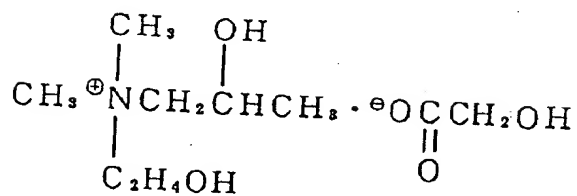
(V-f)



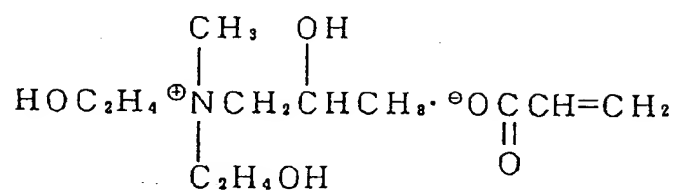
(V-g)



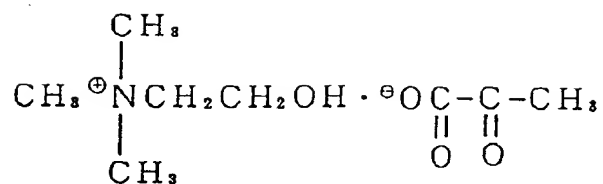
(V-h)



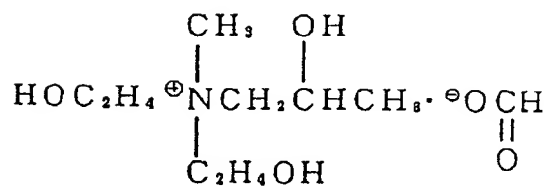
(V-i)



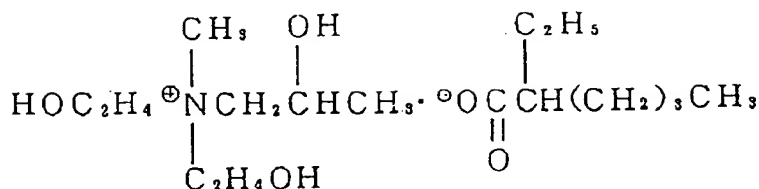
(V-j)



(V-k)



(V-l)



In particular, it is most preferred to use (V-a), (V-b), (V-k) and (V-l).

Other suitable trimerization catalysts are carboxylic acid salts such as potassium 2-ethyl hexanoic acid and sodium acetate; DBU (1,8-diazabicyclo [5,4,0] undecene-7) salts such as phenolic salts and acetic salts; tertiary amines such as 1,3,5-tris-(N,N-dimethyl amino propyl)-s-triazine, and 2,4,6-tris-(dimethyl amino methyl) phenol. Moreover, it is suitable to use alkaline metal salts of aliphatic monocarboxylic acids represented by the formula (VI):

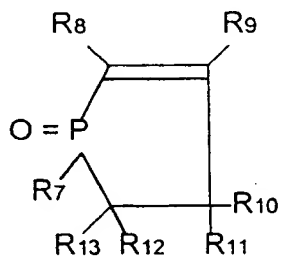


(R₂₀ is hydrogen, substituted or unsubstituted aliphatic hydrocarbons having a C₁-C₇, and M is an alkaline metal).

More than two kinds of the trimerization catalysts listed above may be used in the present invention.

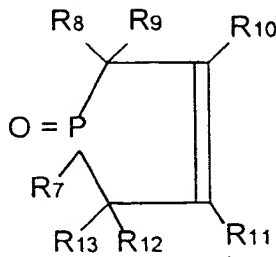
Carbodiimide catalysts containing phospholene oxide are used in the present invention and disclosed in U.S. Pat. No. 3,657,161. As mentioned previously, the catalysts function as a promoter for the formation of carbodiimide linkages and a blowing agent to form carbon dioxide in the foam reaction. An amount of water used in the preparation of the foams is reduced such that the negative effect of the urea linkages, causing high friability of the foams, is diminished. The use of the catalysts in the present invention results that the foams have low flexibility, sufficient compression and adhesion strengths.

It is preferred to use at least one of the following catalysts represented by the formulae (III) and (IV):



(III)

and



(IV)

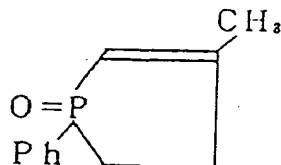
wherein R₇ represents substituted or unsubstituted alkyl, phenyl, naphthyl, or benzyl groups; R₈, R₉, R₁₀, R₁₁, R₁₂, and R₁₃ represent hydrogen, chloride, or alkyl groups having a carbon number of 1 to 4.

Suitable substituted or unsubstituted alkyl groups for R₇ are of straight chains, branching chains, and these types substituted partially by halogen and other functional groups. Such groups are methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, 2-phenylethyl, 2-chloroethyl, and 2-methoxyethyl. It is possible to use substituted or unsubstituted phenyl, benzyl, and naphthyl groups such as o-, p-, or m-tolyl, xylyl, naphthyl, 4-diphenyl, o-, p-, or m-chlorophenyl. Most suitable groups for R₇ are C₁-C₄ alkyl, phenyl, and benzyl. Suitable groups for R₈ to R₁₃ are hydrogen, chloride, methyl, ethyl, propyl, isopropyl, and butyl. Most suitable groups for R₈ to R₁₃ are hydrogen and methyl.

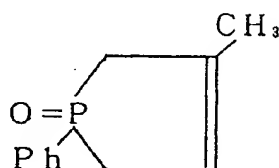
It is referred to use 1-methyl phospholene oxide, 3-methyl-1-phenyl phospholene oxide, 3-methyl-1-benzyl phospholene oxide, 3-methyl-1-ethyl phospholene oxide, 1-phenyl-3-(4-methyl-3-pentyl) phospholene oxide, and 1-phenyl-3-chlorophospholene oxide.

It is most preferred to use 3-methyl-1-phenyl-2-phospholene oxide and 3-methyl-1-phenyl-2-phospholene oxide. The former is represented by the formula (III-a), and the latter is represented by the formula (IV-a).

(III-a)

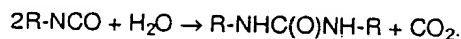


(IV-a)



More than two kinds of these carbodiimide catalysts described above may be used in the present invention.

In the conventional process of the preparation of the modified foams, chlorofluorocarbons were used as blowing agents. However, chlorofluorocarbons are known to damage the ozone layer of the earth; thus, the use of chlorofluorocarbons tends to be totally prohibited in near future. In order to replace the use of chlorofluorocarbons in the preparation, it has been proposed to use carbon dioxide which is obtained from the reaction of the polyisocyanate with water and the carbodiimide reaction (the formation of the carbodiimide linkages). In the former reaction, carbon dioxide is formed in the following chemical reaction:



As mentioned previously, by using the carbon dioxide as a blowing agent, the modified polyisocyanurate foams are prepared in this invention.

However, the urea linkages are formed in the reaction of water and the isocyanate. The linkages are distributed unevenly or ununiformly in the foams and cause coagulation or domain which makes the foams more friable and less compression. Thus there is a serious problem when the foams are used as insulation materials since they adhere to insulation plates improperly.

Nevertheless, the use of the aromatic compounds in the present invention improves all of compression strength, friability, and adhesion strength of the foams. Therefore, the use of the aromatic compounds solves the problem and provides modified polyisocyanurate foams having excellent adhesion strength and high compression strength.

Depending upon necessary physical conditions of the foams, it is preferable to use additives such as: (i) urethane-urea catalysts such as triethylene diamine, dimethyl ethanol amine, triethyl amine, trimethyl aminoethyl ethanol amine, dimethyl amino ethylether, pentamethyl diethylene triamine, N-methyl morpholine, dibutyl tin dilaurate, tin octoate, and lead octoate; (ii) cross-linkers, excluding chain extenders, such as ethylene glycol, propylene glycol, 1,4-butadiol, 1,6-hexadiol, diethylene glycol, triethanol amine, diethanol amine, ethylene diamine, and toluene diamine; (iii) surfactants

such as dimethyl siloxane polyether block co-polymer; (iv) flame-retardants such as triphenyl phosphate, triethyl phosphate, trimethyl phosphate, cresyl diphenyl phosphate, tris cresyl phosphate, tris-(β -chloropropyl) phosphate, tris-(β -chloroethyl) phosphate, trischloroethyl phosphate, trisdichloropropyl phosphate, tris-(2,3-dibromopropyl) phosphate, tris-(bromocresyl) phosphate, melamine, and antimony trioxide; and (v) others like coloring agents.

5 A polyol composition mixture comprising polyols, aromatic compounds, water, trimerization catalysts, and carbodiimide catalysts. These components of the mixture must be selected from the corresponding compounds described previously. It is preferred to add urethane-urea catalysts, surfactants, cross-linkers, flame-retardants, and coloring agents to the polyol composition.

10 A suitable amount of the aromatic compounds ranges from 0.5 to 10.0 wt % against the total weight of the polyol composition (including the aromatic compounds) and the polyisocyanate used in the invention. It is unrecommended to use amounts of the aromatic compounds outside of that range, i.e. less than 0.5 wt % and greater than 10.0 wt %. The former causes a decrease of the number of hard segments in polymer chains the foams; therefore, adhesion strength of the modified foam decreases considerably. The latter causes to increase the number of hard segments; consequently, the foam becomes friable.

15 A preferred amount of the trimerization catalysts ranges at from 0.1 to 10 wt % based upon an amount of solely the polyisocyanate. It is most preferred to use the trimerization catalysts of 0.5 to 5 wt %. On the other hand, it is preferred to use a range from 0.05 to 5 wt % of the carbodiimide catalysts based upon the amount of the polyisocyanate. It is most preferred to use the carbodiimide catalysts of 0.1 to 2 wt %. Furthermore, the relative weight percentage of the trimerization catalysts to the carbodiimide catalysts is preferred to be a range from 0.5 to 20 wt % in the present invention. It is most preferred to use a range of 1 to 10 wt %.

20 A suitable amount of water is within a range from 0.3 % to 1.8 wt % against the total weight of the polyol composition (including the water itself) and the polyisocyanate. It is most preferred to use an amount of water from 0.5 % to 1.5 wt %. By using the suitable amount of water, instead of chlorofluorocarbons, in the present invention, it is possible to set a rise density of the modified foam to be less than 50 kg/m³.

25 These amounts of the polyol mixture components can be changed as to various degrees of desired physical properties of the modified polyisocyanurate foams. But it is required that the isocyanate index, defined by the equivalent ratio of (NCO/OH), is greater than 1.8. In particular, it is preferred to use an isocyanate index range from 1.8 to 5.0 and most preferably from 2.0 to 4.0. In general, as the isocyanate index value increases, flame-retardancy of a polyisocyanurate foam increases.

30 A reaction system used in the present invention consists of the following two parts: (i) an isocyanate or an isocyanate prepolymer comprising an isocyanate and polyols; (ii) a polyol composition consisting of polyols, aromatic compounds, trimerization catalysts, carbodiimide catalysts, water, and additives such as urethane-urea catalysts, cross-linkers, surfactants, flame-retardants, and coloring agents. The parts (i) and (ii) are mixed vigorously at ambient temperature. The mixture may be heated up to 90° C. Suitable materials of plates are prepainted zinc plated steel, prepainted aluminum, 35 prepainted aluminum-zinc alloy plated steel, stainless steel, titanium, and the like. It is possible to use plastics and papers as materials of the plates.

A modified polyisocyanurate foam is prepared by allowing the mixture to foam between the plates. Thus the insulation panels comprise the modified foam and the plates sandwiching the foam. Details of a continuous manufacturing method of the insulation panels are explained in the following.

40 A simple machine for the manufacturing process is shown in Fig. 1; the figure is its cross sectional view. A top plate (1) is transported continuously by two pay-off reels (10a) and then by a pinch roller (12a) in Fig. 1. The top plate (1) goes through a shear (9) and reaches a profiling machine (11a). Similarly, a bottom plate (2) is transported continuously by two pay-off reels (10b) and then by a pinch roller (12b) in Fig. 1. The bottom plate (2) goes through another shear (9) and reaches a profiling machine (11b). At the profiling machine (11a), one end of the top plate (1) is roll-formed into a half part of a male end (32), as shown in Fig.3 (a); the other end is roll-formed into a half part of a female end (30), as shown in Fig.3 (a). Likewise, at the profiling machine (11b), one end of the bottom plate (2) is roll-formed into the other half of the male end (32); the other end is roll-formed into the other half of the female end (31). Surfaces of the plates may be roll-formed with various designs at the profiling machines (11a) and (11b). The top plate (1) is carried farther by a support roller (13). Both the top (1) and the bottom (2) plates meet at a pre-heater (15) to be heated at 30 to 80° C 45 and reach an oven (8).

50 An insulation mixture (4), containing all materials of the foam reaction system mentioned previously, is injected evenly from a spray nozzle (25), equipped in a coating gantry (16), at space between the plates. A typical spray density of the insulation material (4) is from 30 to 60 kg/m³. The gantry (16) can move forward and backward in order to spray the insulation material evenly between the plates. The space between the plates, equivalent of space between the vertical positions of the plates, is adjusted by conveyers (17a) and (17b) that are furnished in the oven (8) and move hydraulically upward and downward.

55 Fig.2 illustrates an enlarged figure of the coating gantry (16) and the conveyers (17a) and (17b) in the oven (8). The figure also illustrates that the insulation mixture (4) is sprayed from the spray nozzle (25) toward the space between the top (1) and the bottom (2) plates. A traveling speed of the plates through the oven (8) and A spraying speed of the nozzle

MR-200: a crude-MDI (product of Nippon Polyurethane Kogyo Sha).

TABLE I

	EXAMPLES					
	1	2	3	4	5	6
Polyols (wt%)						
PS-3152	14.0	12.0	10.5	6.5	11.5	11.0
PS-2352						
Aromatic compounds (wt%)						
BA-P4	1.0	3.0	5.0	10.0		
BA-P8					5.0	
BA-8						5.0
UNILINK-4200						
water (wt%)	0.7	0.7	0.7	0.7	0.7	0.7
Trimerization catalysts (wt%)						
DABCO TMR	1.5	1.5	1.4	1.3	1.6	1.3
DABCO K-15						
SA-NO.1						
Carbodiimide catalysts (wt%)						
2-PMPO	0.5	0.5	0.5	0.5	0.5	0.5
3-PMPO						
Urethane-urea catalyst (wt%)						
DMEA	0.2	0.2	0.2	0.2	0.2	0.2
Surfactant (wt%)						
SH-193	1.0	1.0	1.0	1.0	1.0	1.0
Flame-retardant (wt%)						
FLROL-PCF	3.0	3.0	3.0	3.0	3.0	3.0
Polyol composition sum (wt%)	21.9	21.9	22.3	23.2	23.5	22.7
crude MDI (wt%)	78.1	78.1	77.7	76.8	76.5	77.3
Isocyanate index	3.5	3.5	3.5	3.5	3.5	3.5
Reactivities						
Cream time (s)	11	12	11	11	10	13
Rise time (s)	68	64	67	61	59	63
Free rise density (kg/m ³)	37	38	38	40	34	36
Panel thickness (mm)	35	35	35	35	35	35
Overall density (kg/m ³)	50	50	50	50	50	50
10% compression strength (kg/cm ²)						
Batch	1.6	1.7	1.9	2.1	1.7	1.9
Continuous	1.4	1.6	1.9	1.9	1.4	1.8
Adhesion strength (kg/cm ²)						
Batch	1.3	1.4	1.5	1.7	1.4	1.6
Continuous	1.5	1.6	1.7	1.8	1.5	1.7
Friability (%)						
Batch	48	37	31	28	30	25
Continuous	41	33	28	24	27	23
Dimensional stability (80°Cx3h) (%)	0.3	0.2	0.5	0.2	0.3	0.1
Dimensional stability (-20°Cx3h) (%)	-0.2	-0.1	-0.2	-0.1	-0.1	-0.3
Cutting test (less than 10°C)	Good	Good	Good	Good	Good	Good
Exposure test (for 6 months)	Good	Good	Good	Good	Good	Good

✓
not needed

(25) are adjusted in order to mass-produce the panels (5) efficiently. An original panel (7) consists of the insulation mixture (4) sprayed and the top (1) and bottom (2) plates that sandwich the insulation mixture (4).

Coming back to Fig. 1, the original panel (7) is transported farther and cut by a cutter (20) in order to make insulation panels (5) out of the original panel (7). The insulation panels (5) go through, first, a reject piler (22) that ejects defectives out of a manufacturing line and, second, a main piler (24) that stacks the panels in units.

A cross sectional view the insulation panel (5) is shown in Fig.3 (a). A cross sectional view of the insulation panels (5) connected in series is shown in Fig.3 (b). A plastic foam sealant (31) is inserted at the end of the female end (30), and a piece of moisture preventive tape seals the top of the male end (32). The purpose of these sealing devices is to keep the insulation material (4) inside the panels (5).

It is possible to manufacture insulation panels in batches, instead of using the continuous manufacturing method described above, and insulation panels with only a top plate by using the techniques in the present invention.

EXAMPLES 1-4

Crude-MDI (modified diisocyanate), a polyisocyanate, was used in the present invention. The isocyanate was mixed with a polyol composition mixture comprising a polyol, an aromatic compound, a trimerization catalyst, a carbodiimide catalyst, a urethane-urea catalyst, a surfactant, and a flame-retardant. These components of the polyol mixture are selected from the corresponding compounds described previously. The sum of the mixture and the polyisocyanate was weighed exactly 150 g. The mixture was vigorously stirred with a mechanical drill (2200 rpm, with a 30 mm Ø drill fin) for five seconds. Then a 120 g portion of the mixture was transferred into a wooden box 150 x 150 x 150 mm for free foaming. Cream and rise times of the foam in the box were measured. The cream time is defined as time length between when the portion is stirred and when it starts foaming. The rise time is defined as time length between when the portion is stirred and when it ends foaming. Furthermore, the foam was trimmed such that the volume of the foam became 100 x 100 x 100 mm. A free rise density of the foam was calculated by dividing the weight of the foam by the volume of the foam.

Insulation panels of the modified polyisocyanurate foam were prepared in batches. First, two steel plates with thickness of 0.5 mm were supported with a separated space in a molding tray 260 x 260 x 35 mm heated at 60° C. Second, a 120g portion of the insulation material was poured between of the plates and let the portion foam. Third, the resulting insulation panel was cut into pieces of a size of 100x100x35 mm; a product density of the foam was about 50 kg/m³.

Moreover, insulation panels were prepared by the continuous method described above. Prepainted galvanized steel plates of the insulation panels were heated at 40 to 50° C. An overall density, density of the insulation material used in the continuous method, was 50 kg/m³. The resulting insulation panel dimensioned 35 x 910 mm (thickness x width). A line speed in the continuous method was 8.0 m/min.

Important physical properties of the foams are adhesion strength to plates, 10% compression strength, and friability. They were determined according to the following: (i) JIS A 9514 for the standard of the adhesion strength, (ii) ASTM C 421 for the standard of the friability, and (iii) JIS K 6848 for the standard of the 10% compression strength, respectively. Furthermore, additional tests such as dimensional stability, cutting, and exposure tests were applied to examine qualities of insulation panels. Specific definitions of these tests are explained by the following: (iv) the dimensional stability test is examinations of the thickness of a panel at two different temperatures: high (80° C) and low (-20° C); (v) the slicing test is an examination of the presence of cracks in the panel and detachments of the foam from the plates after the insulation panel cooled at 10° C is cut; and (vi) the exposure test is an examination of cracks in the panel and detachments of the foam from the plates after the insulation panel was exposed outdoor for 6 months. These physical measurements and tests were applied to the foams prepared by both batch and continuous methods.

For modified polyisocyanurate foams prepared in examples 1-4, an amount of the aromatic compound BA-P4 was increased from 1.0 % to 10.0 wt %. As a result, values of the adhesion strength and 10% compression strength of the foams were increased when the amount of the aromatic compound was increased. The friability of the foams was also improved. Thus, it follows that the use of the aromatic compound as a chain extender contributes to the improvement of the friability, adhesion strength, and compression strength of the foams. Insulation panels prepared in examples had high dimensional stability and no cracks and detachments from the plates. No chlorofluorocarbon was used in these examples.

EXAMPLES 5-7

A series of modified polyisocyanurate foams was prepared by the same process explained previously except with the uses of different aromatic compounds: namely, BA-P8, BA-8, and UNILINK-4200. Insulation panels prepared in examples had high dimensional stability and no cracks and detachments from the plates.

The following TABLE I describes ingredients and amounts of the foams prepared in examples 1-6, values of the physical properties necessary to determine the qualities of the foams and results of the tests for the insulation panels prepared in these examples.

The following list summarizes abbreviated compound names used in examples and comparative examples:

(product of Toray-Dowcorning-Silicone Corporations).

FIROL-PCF; a flame-retardant of tris-(β -chloropropyl) phosphate (product of Akzo-Kashima Corporations).

DEG; an aliphatic compound of diethylene glycol.

TEG: an aliphatic compound of triethylene glycol.

CFC-11: a chlorofluorocarbon of trichlorofluoro methane.

EXAMPLES 8-10

A series of modified polyisocyanurate foams was prepared by the same process explained previously except with the uses of different isocyanurate-trimerization catalysts: namely, DABCO TMR, DABCO K-15 and SA-NO.1. Insulation panels prepared in examples had high dimensional stability and no cracks and detachments from the plates.

EXAMPLES 11-12

Two more modified polyisocyanurate foams were prepared by the same process explained previously except by changing amounts and types of polyols: namely, PS-3152 and PS-2352. Comparing the results of examples 2 and 11, the friability improved significantly as an amount of the polyol PS-3152 increased from 12.0 % to 20.0 wt %. Therefore, it follows that the increase in the polyol rate used improves the friability of the foam. Insulation panels prepared in examples had high dimensional stability and no cracks and detachments from the plates.

The following TABLE II describes ingredients and amounts for the foams prepared in examples 7-12, values of the physical properties of the foams and results of the test for the insulation panels.

5 PS-3152: a polyester polyol at the hydroxyl value of 315 (product of STEPAN Corporation).

10 PS-2352: a polyester polyol at the hydroxyl value of 235 (product of STEPAN Corporation).

NP-300: a polyether cross-linker at the hydroxyl value of 767 (product of Sanyokasei Kogyo Sha).

15 BA-P4: an aromatic compound represented by the formula (I) (a) (product of Nippon Nyukazai Sha).

20 BA-P8: an aromatic compound represented by the formula (I) (b) (product of Nippon Nyukazai Sha).

25 BA-8: an aromatic compound represented by the formula (I) (c) (product of Nippon Nyukazai Sha).

30 UNILINK-4200: an aromatic compound represented by the formula (II-a) (product of UOP Corporation).

DABCO TMR: a trimerization catalyst represented by the formula (V) (a) (product of Airproducts Corporation).

35 DABCO K-15: a trimerization catalyst of potassium 2-ethyl hexanoate (product of Airproducts Corporation).

40 SA-NO.1: a trimerization catalyst of DBU (1,8-diazabicyclo [5,4,0] undecene-7) phenolic salt (product of Sanapro Corporation).

45 2-PMPO: a carbodiimide catalyst of 3-methyl-1-phenyl-2-phosphorous oxide.

50 3-PMPO: a carbodiimide catalyst of 3-methyl-1-phenyl-3-phosphorous oxide.

DMEA: a urethane-urea catalyst of dimethyl ethanol amine.

55 SH-193: a surfactant of dimethyl siloxane polyether block co-polymer

TABLE II

	EXAMPLES					
	7	8	9	10	11	12
Polyols (wt%)						
PS-3152	9.0	12.0	12.0	12.0	20.0	
PS-2352						15.0
Aromatic compounds (wt%)						
BA-P4		3.0	3.0	3.0	3.0	3.0
BA-P8						
BA-8						
UNILINK-4200	5.0					
water (wt%)	0.7	0.7	0.7	0.7	0.7	0.7 ✓
Trimerization catalysts (wt%)						
DABCO TMR	1.3			1.5	1.3	1.6
DABCO K-15		1.7				
SA-NO.1			1.4			
Carbodiimide catalysts (wt%)						
2-PMPO	0.5	0.5	0.5		0.5	0.5
3-PMPO				0.5		
Urethane-urea catalyst (wt%)						
DMEA	0.2	0.2	0.2	0.2	0.3	0.2
Surfactant (wt%)						
SH-193	1.0	1.0	1.0	1.0	1.0	1.0 ✓
Flame-retardant (wt%)						
FLROL-PCF	3.0	3.0	3.0	3.0	3.0	3.0
Polyol composition sum(wt%)	20.7	22.1	21.8	21.9	29.8	25.0 ✓
crude MDI (wt%)	79.3	77.9	78.2	78.1	70.2	75.0
Isocyanate index	3.5	3.5	3.5	3.5	2.5	3.5
Reactivities						
Cream time (s)	12	12	12	10	11	12
Rise time (s)	61	62	65	60	58	61
Free rise density (kg/m ³)	36	37	40	36	38	38
Panel thickness (mm)	35	35	35	35	35	35
Overall density (kg/m ³)	50	50	50	50	50	50
10%compression strength (kg/cm ²)						
Batch	1.8	1.8	1.7	1.7	1.6	1.7
Continuous	1.8	1.6	1.7	1.9	1.4	1.6
Adhesion strength (kg/cm ²)						
Batch	1.6	1.3	1.3	1.6	1.2	1.6
Continuous	1.7	1.7	1.7	1.8	1.4	1.7
Friability (%)						
Batch	25	34	29	32	25	29
Continuous	23	31	29	30	22	26
Dimensional stability (80°Cx3h) (%)	0.4	0.2	0.1	0.1	0.3	0.2
Dimensional stability (-20°Cx3h) (%)	-0.1	-0.2	-0.3	-0.1	-0.2	-0.2
Cutting test (less than 10°C)	Good	Good	Good	Good	Good	Good
Exposure test (for 6 months)	Good	Good	Good	Good	Good	Good

ASTM
C 421

Modified polyisocyanurate foams prepared in the following comparative examples were provided by the same preparation process explained previously in examples discussed above except that at least one component of the polyol mixture was either missing or changed. Each sum of the ingredients in these comparative examples was also weighed

exactly 150 g. Cream times, rise times, and free rise densities of the foams were measured by using the same methods mentioned previously. Adhesion strengths, 10% compression strengths, and friabilities of the foams were measured by using the same standards. Qualities of the insulation panels were evaluated by the tests in examples.

5 COMPARATIVE EXAMPLE 1

No carbodiimide catalyst was used in this example. A free rise density of the resulting foam in this example was more than 50 kg/m³, due to an insufficient amount of carbon dioxide. Thus the foam had high density so that the manufacture of insulation panels by both continuous and batch methods were extremely difficult.

10

COMPARATIVE EXAMPLE 2

In this example also, no carbodiimide catalyst was used. Instead, an amount of water was increased from 0.7 % to 1.2 wt % in order to compensate an amount of carbon dioxide that the use of carbodiimide catalyst would have formed.

15

However, significant urea linkages were formed in this preparation, resulting in an increase of coagulation in the foam. Comparing this result with the ones in examples 1-12, the foam became extremely friable and the compression strength and adhesion strength of the foam were considerably reduced. Detachments of the foam from the plates of insulation panel prepared in this example were observed in both the cutting and exposure tests.

20 COMPARATIVE EXAMPLE 3

No aromatic compound was used in this example. The resulting foam showed low compression strength and poor adhesion strength compared with those physical properties in examples 1-12. Cracks on the insulation panel prepared in this comparative example were observed in both the cutting and exposure tests. The friability was also increased in this example.

25

COMPARATIVE EXAMPLE 4

No water was used in this example. Instead, an excess amount of carbodiimide catalyst was used to supply enough carbon dioxide in the reaction. Comparing this result with the ones in examples 1-12, the resulting foam in this comparative example had insufficient compression strength and adhesion strength required for insulation panels. The dimensional stability of the insulation panel prepared in this comparative example was weakened at least by factor of 10. Considerable shrinkage of the panel was observed by the exposure test.

30 COMPARATIVE EXAMPLES 5-6

Aliphatic compounds, instead of the aromatic compounds, were used in these comparative examples. The foams prepared without the use of aromatic compounds had insufficient compression strength and adhesion strength required for insulation panels. These comparative examples, together with comparative example 3, demonstrated importance of the use of the aromatic compounds in the present invention. The dimensional stability of the insulation panel prepared in this comparative example was weakened at least by factor of 5. Cracks in the panel were observed by the cutting and exposure tests.

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TABLE III

	COMPARATIVE EXAMPLES					
	1	2	3	4	5	6
<u>Polyols (wt%)</u>						
PS-3152	12.0	5.0	14.5	22.0	6.5	8.5
PS-2352						
NP-300						
<u>Aromatic compounds (wt%)</u>						
BA-P4	3.0	3.0		3.0		
<u>Aliphatic compounds (wt%)</u>						
DEG					3.0	
TEG						3.0
water (wt%)	0.7	1.2	0.7		0.7	0.7
<u>Fluorocarbon</u>						
CFC-11						
<u>Trimerization catalysts (wt%)</u>						
DABCO TMR	1.5	1.7	1.5	1.5	1.5	1.6
<u>Carbodiimide catalysts (wt%)</u>						
2-PMPO			0.5	1.8	0.5	0.5
<u>Urethane-urea catalyst (wt%)</u>						
DMEA	0.2	0.3	0.2	0.4	0.2	0.2
<u>Surfactant (wt%)</u>						
SH-193	1.0	1.0	1.0	1.0	1.0	1.0
<u>Flame-retardant (wt%)</u>						
FLROL-PCF	3.0	3.0	3.0	3.0	3.0	3.0
Polyol composition sum(wt%)	21.4	15.2	21.5	32.7	16.4	18.5
crude MDI (wt%)	78.6	84.8	78.5	67.3	83.6	81.5
Isocyanate index	3.5	3.5	3.5	3.5	3.5	3.5
<u>Reactivities</u>						
Cream time (s)	11	10	11	14	8	10
Rise time (s)	58	52	63	67	59	63
Free rise density (kg/m ³)	52	38	37	36	35	38
Panel thickness (mm)	--	35	35	35	35	35
Overall density (kg/m ³)	--	50	50	50	50	50
<u>10%compression strength (kg/cm²)</u>						
Batch	--	1.3	1.0	0.7	0.7	0.6
Continuous	--	1.2	1.1	0.9	0.8	0.7
<u>Adhesion strength (kg/cm²)</u>						
Batch	--	0.2	0.8	0.6	0.5	0.5
Continuous	--	0.4	1.2	0.8	0.7	0.6
<u>Friability (%)</u>						
Batch	--	85	58	44	56	58
Continuous	--	78	58	38	52	50
Dimensional stability (80°Cx3h) (%)	--	-0.2	0.5	-4.6	-2.4	-2.6
Dimensional stability (-20°Cx3h)(%)	--	-0.5	-0.3	-2.3	-1.1	-1.8
Cutting test (less than 10°C)	--	detached	cracked	good	cracked	cracked
Exposure test (for 6 months)	--	detached	cracked	shrunk	cracked	cracked

Table III sets forth ingredients and amounts for comparative examples 1-6, values of the physical properties of the foams and results of the tests for the insulation panels prepared in these comparative examples.

COMPARATIVE EXAMPLES 7-8

Neither aromatic compound nor carbodiimide catalyst was used in these comparative examples. Comparing these results with the ones in examples 1-12, the foams in these comparative examples increased the friable and the compression strength and adhesion strength of the foams were significantly low. The dimensional stability of the insulation panel prepared in this comparative example was weakened at least by factor of 5. Cracks in the panel were observed by the cutting and exposure tests.

An amount of water was increased in these comparative examples to supply carbon dioxide which was not formed due to the absence of a carbodiimide catalyst. Urea linkages were also formed by the reaction between polyisocyanate and water. In effect, the presence of the linkages in the foams caused to lower the compression strength and the adhesion strength of the foams.

COMPARATIVE EXAMPLE 9

In this example, a fluorocarbon was used as a blowing agent. The foam prepared without fluorocarbons in examples 1-12, particularly the example 2, was as good as the foam prepared in this comparative example.

The following TABLE IV lists ingredients and amounts used in the preparations of the foams for comparative examples 7-9, values of the physical properties of the foam and results of the tests for the insulation panels prepared in this comparative example.

TABLE IV

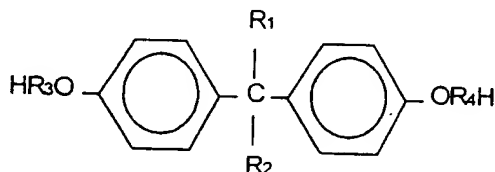
INGREDIENTS	COMPARATIVE EXAMPLES		
	7	8	9
<u>Polyols (wt%)</u>	7.5		17.0
PS-3152		9.0	
PS-2352			3.0
NP-300			
<u>Aromatic compounds (wt%)</u>			3.0
BA-P4			
BA-P8			
BA-8			
UNILINK-4200			
water (wt%)	1.2	1.2	0.2
<u>Fluorocarbon</u>			7.0
CFC-11			
<u>Trimerization catalysts (wt%)</u>	1.7	1.8	2.0
DABCO TMR			
<u>Carbodiimide catalysts (wt%)</u>			
2-PMPO			
<u>Urethane-urea catalyst (wt%)</u>	0.3	0.3	0.2
DMEA			
<u>Surfactant (wt%)</u>	1.0	1.0	1.0
SH-193			
<u>Flame-retardant (wt%)</u>	3.0	3.0	3.0
FLROL-PCF			
Polyol composition sum(wt%)	14.7	16.3	23.4
crude MDI (wt%)	85.4	83.7	76.6
Isocyanate index	3.5	3.5	3.5
<u>Reactivities</u>			
Cream time (s)	9	11	12
Rise time (s)	54	61	57
Free rise density (kg/m ³)	37	37	40
Panel thickness (mm)	35	35	35
Overall density (kg/m ³)	50	50	50
<u>10% compression strength (kg/cm²)</u>			
Batch	0.7	0.6	1.8
Continuous	0.8	0.7	2.0
<u>Adhesion strength (kg/cm²)</u>			
Batch	0.2	0.3	1.4
Continuous	0.3	0.4	1.7
<u>Friability (%)</u>			
Batch	89	88	28
Continuous	84	81	21
Dimensional stability (80°Cx3h) (%)	-2.6	-2.3	1.3
Dimensional stability (-20°Cx3h) (%)	-1.8	-1.1	-0.4
Cutting test (less than 10°C)	detached	detached	Good
Exposure test (for 6 months)	detached	detached	Good

The features disclosed in the foregoing description, in the claims and/or in the accompanying drawings may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

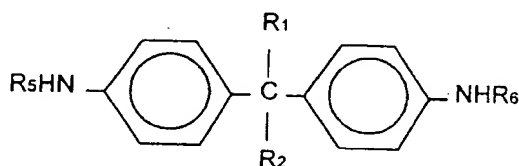
Claims

1. An heat insulation panel comprising a foam of modified polyisocyanurate which is provided by a reaction of a polyisocyanate, a polyol, and water in the presence of a first catalyst promoting isocyanurate linkages and a second catalyst of phospholene oxide promoting carbodiimide linkages, wherein an aromatic compound is added in the above reaction, said aromatic compound being represented by one of the following formula (I) and (II):

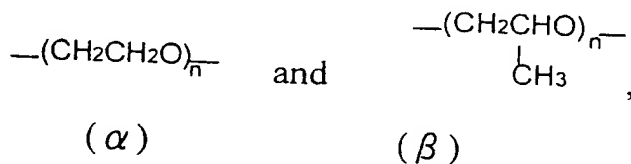
(I)



(II)



wherein R_1 and R_2 represent one of H and $-\text{CH}_3$, R_3 and R_4 represent one of the following (α) and (β):

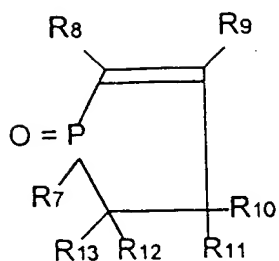


R_5 and R_6 represent a C_1 - C_4 alkyl group, and n represents an integer from 1 to 4.

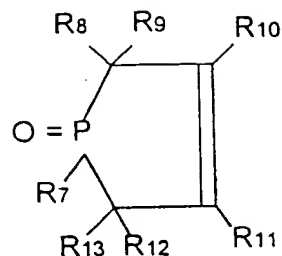
2. An insulation panel of claim 1, wherein said second catalyst is at least one of those represented by the following formulae (III) and (IV):

(III)

(IV)



and



wherein R₇ represents substituted or unsubstituted alkyl, phenyl, naphthyl, or benzyl groups; R₈, R₉, R₁₀, R₁₁, R₁₂, and R₁₃ represent hydrogen, chloride, or alkyl group having a carbon number of 1 to 4.

3. An insulation panel of claim 1, wherein said aromatic compound is incorporated in an amount of 0.5 to 10.0 % by weight based upon a total amount of said aromatic compound, polyisocyanate, polyol, catalysts, and water.
4. A insulation panel manufactured by the following steps of:
 - a) preparing a mixture of a polyisocyanate, a polyol, water, catalysts, and an aromatic compound,
 - b) injecting said mixture between a pair of spaced plates, and
 - c) reacting said mixture between said spaced plates, so as to provide a foam of modified polyisocyanurate adhered to said plates.
5. An insulation panel of claim 4, wherein said aromatic compound is incorporated in an amount of 0.5 to 10.0 % by weight based upon a total amount of said aromatic compound, polyisocyanate, polyol, catalysts, and water.

FIG. 1

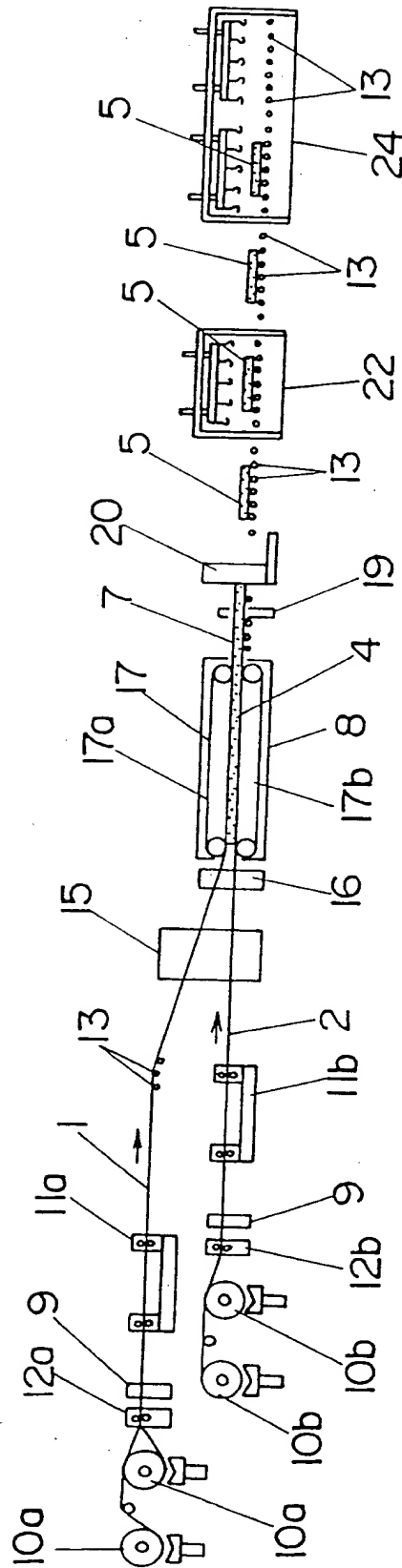
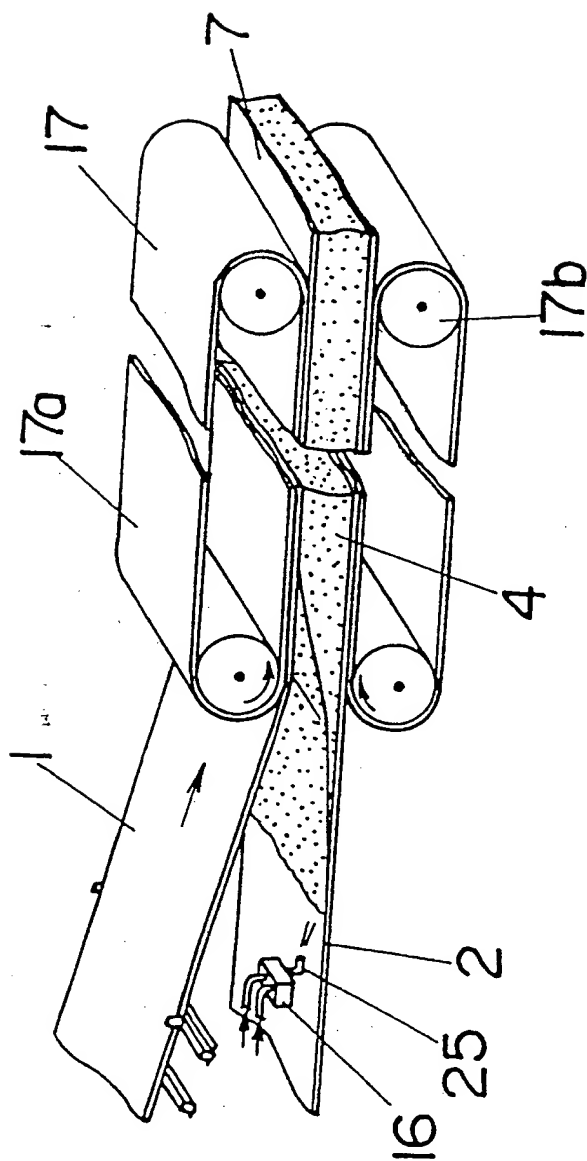


FIG. 2



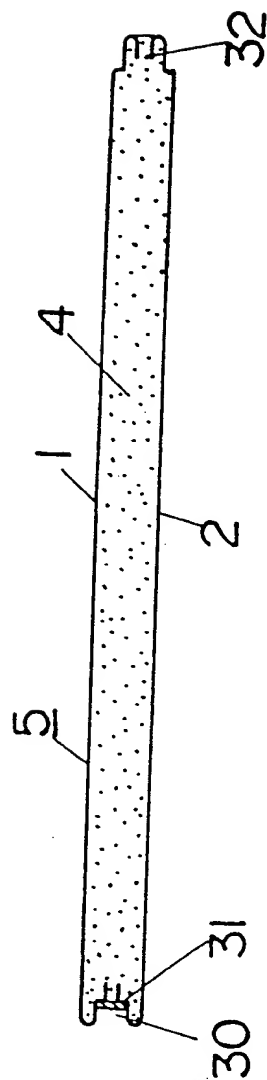


FIG. 3 (a)

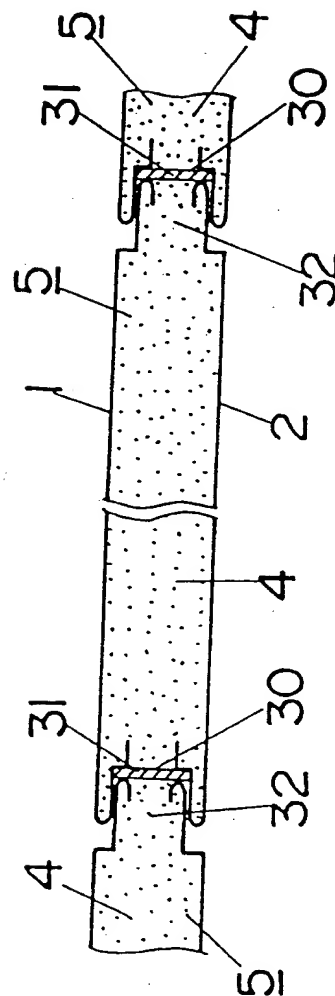


FIG. 3 (b)

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(54) **Heat insulation panels manufactured from modified polyisocyanurate foams**

(57) Heat insulation panels made from plates and the modified polyisocyanurate foams provided by a reaction of a polyisocyanate with a polyol composition mixture comprising a polyol, water, a trimerization catalyst, a carbodiimide catalyst, and an aromatic compound used as a chain extender. An amount of the aromatic compound used in the preparation is 0.5 to 10.0 % by weight with respect to a total weight of the polyisocyanate and the polyol mixture.

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X	EP 0 594 181 A (NISSHINBO INDUSTRIES) * the whole document; in particular: page 3, line 37-58*	1,2	C08G18/02 C08G18/16 C08G18/66 C08G18/65 C08G18/79
A	FR 2 272 114 A (BASF WYANDOTTE) * page 2, line 22 - page 3, line 9; claims 1,4; examples 25-36 *	1	
A	US 3 919 128 A (BALDINO ET AL) 11 November 1975 * column 4, line 46 - column 6, line 58 * * column 11, line 31 - line 51; claims 1-4 *	1	
A	US 5 223 551 A (GATTUSO ET AL) * column 2, line 48 - column 5, line 11; claims 1,3 *	1	
A	CELLULAR POLYMERS, vol. 12, no. 1, 1993, SHREWSBURY, SHROPSHIRE, GB, pages 46-59, XP000362457 SCOTT ET AL: "THE USE OF SECONDARY AROMATIC DIAMINES IN RIGID ISOCYANURATE-BASED FOAMS"	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08G
D,A	EP 0 381 324 A (IMPERIAL CHEMICAL INDUSTRIES) * page 2, line 36 - page 6, line 7; claims *	1,2	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 December 1996	Examiner Bourgonje, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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